Structural and Ferroelectric Characterizations of $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ Multifunctional Ceramics

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Abstract

Pellets were prepared from a powder mixture of 80 mol. % of potassium niobate ($KNbO_3$) and 20 mol. % of potassium magnesium fluoride ($KMgF_3$). The pellets were sintered at 900 ° C for 15 h in gold sealed tubes. The structural transformations in the obtained oxyfluoride $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ were checked by X-ray diffraction (XRD) from room temperature to 525 ° C. The phase transitions were investigated by dielectric measurements (DE), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Three crystallographic phase transitions were observed by DE at T_1 = 25 ° C, T_2 = 125 ° C and T_C = 270 ° C respectively corresponding, on heating, to the successive structural changes rhombohedral - orthorhombic - orthorhombic - tetragonal. The two phase transitions at T_2 and T_C were confirmed by DTA, DSC and XRD. The paraelectric phase at $T > T_C$ was found to be tetragonal whereas pure $KNbO_3$ exhibits a cubic paraelectric phase. A maximum of the dielectric permittivity ε'_r of about 1800 and a dissipation factor tanδ of 43 % are observed at T_C. The ceramic $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ could be of interest in various electronic devices and particularly for electromechanical conversion owing to its high values of T_C and tanδ.

Keywords

Ceramic; $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$; Phase Transitions

Introduction

Ferroelectrics ABO_3 with the perovskite-type structure and their solid solutions are of considerable importance for technological applications due to their piezoelectric, pyroelectric, ferroelectric, optical and nonlinear optical properties. Nowadays, ABO_3 ceramics become the "heart" of smart systems in many electronic devices with artificial intelligence.

Up to now, lead-containing materials such as $PbTiO_3$, $Pb(Zr,Ti)O_3$ or PZT and $Pb(Mg,Nb)O_3$ or PMN have dominated the market of microelectronic components. Nevertheless, lead (Pb) is known to be toxic and may seriously affect human health and natural environment. Therefore, extensive research is actually oriented towards the replacement of lead-based ceramics with lead-free materials. Alkaline niobates and, in particular, potassium niobate $KNbO_3$ and its solid solutions have been found to be the most promising lead-free ferroelectric compounds. However, the most important problem with pure potassium niobate is the difficulty of sintering dense ceramics at low temperature. Furthermore, when sintering is performed in free-air, the chemical composition could not be controlled due to the volatilization of potassium oxyde K_2O. Therefore, various additives (oxides or double oxides) were used to improve the sintering and properties of $KNbO_3$. In this way, we undertook this study because the number of published articles on oxifluorides deriving from potassium niobate is very limited.

The phase transitions of $KNbO_3$ were investigated either on single crystals or on ceramics by a lot of researchers, using various techniques. Whatever the method used, the same sequence of crystallographic transformations was reported by the different authors.

At room temperature, potassium niobate is a well known ferroelectric-ferroelastic material and, like $BaTiO_3$, $KNbO_3$ undergoes three successive phase transitions of first order with the same sequence of structural changes:

Rhombohedral ⟷ *Orthorhombic* ⟷ *Tetragonal* ⟷ *Cubic*

R3m Amm2 P4mm Pm3m

The rhombohedral, orthorhombic and tetragonal phases are ferroelectric. According to G. Shirane, H. Danner, A. Pavlovic and R. Pepinsky, the structural transformations occur at T_1 = - 10 ° C, T_2 = 225 ° C and T_C = 435 ° C respectively. The ferroelectric Curie

temperature of $KNbO_3$ (435 ° C on heating) is much higher than that of $BaTiO_3$ (120 ° C).

During more than two decades, most of the published papers on $KNbO_3$ were devoted to the understanding of its phase transitions and their modelling. The investigations were generally carried out on single crystals using various spectroscopic techniques: XRD, IR, RAMAN, XAFS and EXAFS. The controversies between the numerous studies were about the description of these phase transitions and two main theoretical models have been proposed:

- The displacement model
- The order – disorder model

More recently, a detailed theory, called "eight - site model", has been built up. This model is based on the coexistence of relaxation, order – disorder and soft phonon displacement modes in potassium niobate phase transitions. The different models have been well summarised by S. Tinte, M. Sepliarsky, M. G. Stachiotti, R.L. Migoni and G.O. Rodriguez. The three models are not in contradiction one with another but are complementary. So, for the modelling of the phase transitions in $KNbO_3$ the three mechanisms have to be considered.

According to the first model, Nb^{5+} ions are displaced from the centers of NbO_6 octahedra along the polar axes: three-fold axis in rhombohedral phase, two-fold axis in orthorhombic phase and four-fold axis in tetragonal symmetry. In the second model the phase transitions mechanism is explained in terms of order – disorder in niobium positions in the crystallographic lattice. With increasing temperature, the degree of order – disorder nature of the phase transitions increases.

L.A. Bugaev, V.A. Shuvaeva, I.B. Alekseenko, K.N. Zhuchkov and R.V. Vedrinskii studied the local structure of NbO_6 octahedra in the orthorhombic phase of a $KNbO_3$ crystal using EXAFS and found that the preferential direction of displacement of niobium ions from the centrosymmetric positions is the polar two-fold axis.

V.A. Shuvaeva, K. Yanagi, K. Yagi, K. Sakaue and H. Tarauchi reported that all phase transitions in $KNbO_3$ are governed by both displacive and order – disorder mechanism. The rhombohedral–orthorhombic phase transition is considered as essentially a displacive type, while the order–disorder mode is dominant in the tetragonal –cubic phase transition.

On the other hand, the photorefractive characteristics of potassium niobate make it of interest for optoelectrical applications as well as a post PZT material. Orthorhombic $KNbO_3$ is especially interesting for NLO applications owing of its large value of the spontaneous polarization at room temperature. More recently, several authors have investigated the photocatalytic properties of potassium niobate and found that this material could be used as photocatalyst in the decomposition of H_2O into H_2 and O_2 to get clean and high energy.

In previous works we studied the $KNbO_3$ - $BaLiF_3$, $KNbO_3$ - $NaMgF_3$ and $KNbO_3$ - $KMgF_3$ chemical systems and three oxyfluoride solid solutions with perovskite structure were obtained:

- $K_{1-x}Ba_x(Nb_{1-x}Li_x)O_{3-3x}F_{3x}$ $(0 \le x \le 0.75)$
- $K_{1-x}Na_x(Nb_{1-x}Mg_x)O_{3-3x}F_{3x}$ $(0 \le x \le 0.30)$
- $K(Nb_{1-x}Mg_x)O_{3-3x}F_{3x}$ $(0 \le x \le 0.40)$

On the other hand, we investigated in detail the (1-x) $KNbO_3$ – $xTaO_2F$, (1-x)$KNbO_3$ – $xNbO_2F$ and (1-x)$KNbO_3$ – $xTiOF_2$ mixed systems. As results:

- For TaO_2F additive, no solid solution or intermediate phase appeared over all the composition range.
- When NbO_2F is added to $KNbO_3$, an intermediate phase $K_{1-x}NbO_{3-x}F_x$ with tetragonal tungsten bronze-type structure appeared in the composition range $0.4 \le x \le 0.6$.
- The addition of $TiOF_2$ to $KNbO_3$, showed the formation of a unique phase corresponding to x = 0.4 with formula $K_{0.6}(Nb_{0.6}\ Ti_{0.4})O_{2.2}F_{0.8}$ or $K_3Nb_3Ti_2O_{11}F_4$. This one is isomorph to $Ba_2NaNb_5O_{15}$ and exhibits the tetragonal tungsten bronze structure. $K_3Nb_3Ti_2O_{11}F_4$ crystal could be of interest in laser technology thanks to its optical properties.

Our present study is axed on the sintering of $KNbO_3$–based ceramics with the aid of 20 mol. % of $KMgF_3$ then, the investigation of dielectric properties and phase transitions in the obtained oxyfluoride $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$. Such bulk ceramic, sintered in sealed tube, will be exempt from hydroxyl ions (OH^-) and could be used as a target for thin films deposition with controlled composition.

Experimental Procedures

K_2CO_3, Nb_2O_5, KF and MgF_2 used in the samples preparation were MERCK products with purity

greater than 99.99%. $KNbO_3$ and $KMgF_3$ were synthesized by the conventional solid state reaction at 850 ° C and 700 ° C respectively with a heating rate of 150 ° $C.h^{-1}$:

$$K_2CO_3 + Nb_2O_5 \longrightarrow 2\ KNbO_3 + CO_2$$

$$KF + MgF_2 \longrightarrow KMgF_3$$

K_2CO_3 and Nb_2O_5 mixture was calcined in a gold crucible in air for 15 h whereas KF + MgF_2 powder was heated in a gold sealed tube under argon gas (Ar) for 6 h. Finally, 80 mol. % of $KNbO_3$ were thoroughly mixed with 20 mol. % of $KMgF_3$ and ground. This powder mixture was pressed into pellets of 9 mm in diameter and about 1 mm thickness. The pellets were then sintered at 900 ° C for 15 h in gold sealed tubes under dry helium (He):

$$0.80\ KNbO_3 + 0.20\ KMgF_3 \longrightarrow K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$$

Dielectric characterizations were performed on disks whose faces were metallised with gold (Au) to make capacitors. The real permittivity ε'_r and the dielectric losses tanδ were measured as a function of temperature at 1 kHz between – 100 ° C and 450 ° C using an automatic capacitance bridge.

X-ray diffraction analyses were carried out at room temperature with a PHILIPS PW 1710 diffractometer using the $CuK_{\alpha 1}$ radiation (λ = 1.5406 Å) and pure silicon (Si) as internal standard. GUINIER - SIMON spectra were collected from 25 ° C up to 525 ° C.

Differential scanning calorimetry analyses (DSC) were carried out on heating and cooling under nitrogen gas with a PERKIN-ELMER apparatus (SENDON DSC 7), in the temperature range 25 – 600 ° C, with a rate of 10 ° $C.min^{-1}$.

Differential thermal analyses (DTA) are performed on heating and cooling with a NETZSCH 404S apparatus. The ceramic is crushed into fine powder which is then introduced in a platinum tube, sealed under dry argon. The analyses are carried out in the temperature range 25 – 1000 ° C with a rate of 10 ° $C.min^{-1}$.

More details on sample's preparation and characterizations could be found in our previous paper on $Na_{0.90}K_{0.10}(Nb_{0.90}\ Mg_{0.10})O_{2.70}F_{0.30}$ ferroelectric ceramics.

Results and Discussion

The shrinkage $\Delta\phi / \phi$ of pure $KNbO_3$ sintered at 900 ° C for 15 h is lower than that of $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ sintered in the same conditions :

$$\Delta\phi / \phi\ (KNbO_3) = 1\ \%$$

$$\Delta\phi / \phi\ (K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}) = 5\ \%$$

After sintering in sealed tube, the oxyfluoride ceramic is exempt from OH^- ions in the crystallographic lattice and stable in free air whereas most of alkali metal compounds are hygroscopic and disintegrate in air within a short time.

Room-temperature spectra of $KNbO_3$ and $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ are quite similar to each other and show orthorhombic symmetry (FIG. 1).

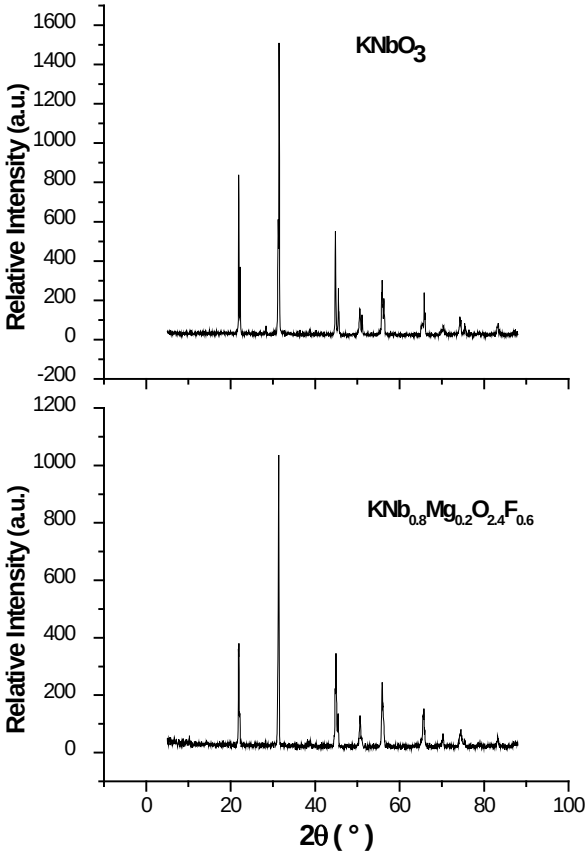

FIGURE 1 XRD PATTERNS OF $KNBO_3$ AND $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ AT ROOM TEMPERATURE

The unit cell parameters of the two samples are very proach ones an others:

$$KNbO_3 :\ a = 3.974\ Å\ ;\ b = 5.695\ Å\ ;\ c = 5.722\ Å$$

$$K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6} :\ a = 3.981\ Å\ ;\ b = 5.696\ Å\ ;\ c = 5.713\ Å$$

The NbO_6 and MgF_6 octahedra have practically the same size, the size increase from Nb^{5+} to Mg^{2+} being compensated by the size decrease from O^{2-} to F^- ($r_{Nb^{5+}}$ = 0.64 Å ; $r_{Mg^{2+}}$ = 0.72 Å ; $r_{O^{2-}}$ = 1.35 Å ; r_{F^-} = 1.228 Å).

Therefore there is no significant change in the lattice parameters a, b and c.

The temperature dependence of the real permittivity ε'_r, its inverse ε'^{-1}_r and the dielectric losses tanδ, on cooling, are depicted in Fig. 2.

Three dielectric anomalies are clearly observed as well on ε'_r - T as on ε'^{-1}_r - T or on tanδ - T curves at T_1 = 25 ° C, T_2 = 125 ° C and T_C = 270 ° C respectively. The discontinuous variation of ε'^{-1}_r with temperature is typical of first order phase transitions. The first and second ones appear as shoulders on ε'_r - T plot whereas a broad peak with ε'_{rmax} ~ 1800 is detected at the ferroelectric Curie temperature T_C. The value of tanδ at T_C is ~ 0.43 (Fig. 2).

In comparison with pure $KNbO_3$ which exhibits sharp peaks of the dielectric constant, $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ displays diffuse phase transitions with a rounded maximum of the permittivity at T_C (Fig. 2). The broadness of ε'_{rmax} is ascribed to the double occupation of B – crystallographic sites in ABO_3 perovskites by ions of different valences (Nb^{5+}, Mg^{2+}) and a gradient of composition in the ceramic's grains.

The ferroelectric Curie temperature of $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ ceramic T_C = 270 ° C is much lower than that of pure $KNbO_3$ T_C = 435 ° C. This result agrees quite well with our previous works on ferroelectric oxifluorides. It is especially attributed to the anionic substitution O^{2-} - F^- which induces a covalence diminishing on the chemical bonds (polarization coefficient: F^- = 0.81 x 10^{-24} cm^3 ; O^{2-} = 3.88 x 10^{-24} cm^3). Furthermore, taking into account the displacive model in ferroelectric materials, the substitution of Mg^{2+} to Nb^{5+} reduces the displacement Δz along the polar axis in the MgO_6 and MgF_6 octahedra because the size of magnesium ion (0.72 Å) is larger than that of niobium ion (0.64 Å). Therefore, the Curie temperature decreases according to the empirical relationship:

$$T_C = 2 \times 10^4 (\Delta z)^2$$

The monotonous thermal variation of dielectric losses between room temperature and ~ 200 ° C is probably related to a soft mode displacement of the various ions in the lattice. The strong increase of tanδ beyond 300 ° C is due to the ionic conductivity.

As DE results, the admixture of $KMgF_3$ to $KNbO_3$ maintains the three phase transitions but increases the rhombohedral – orthorhombic transition temperature T_1 and decreases the transition temperatures at T_2 and T_C.

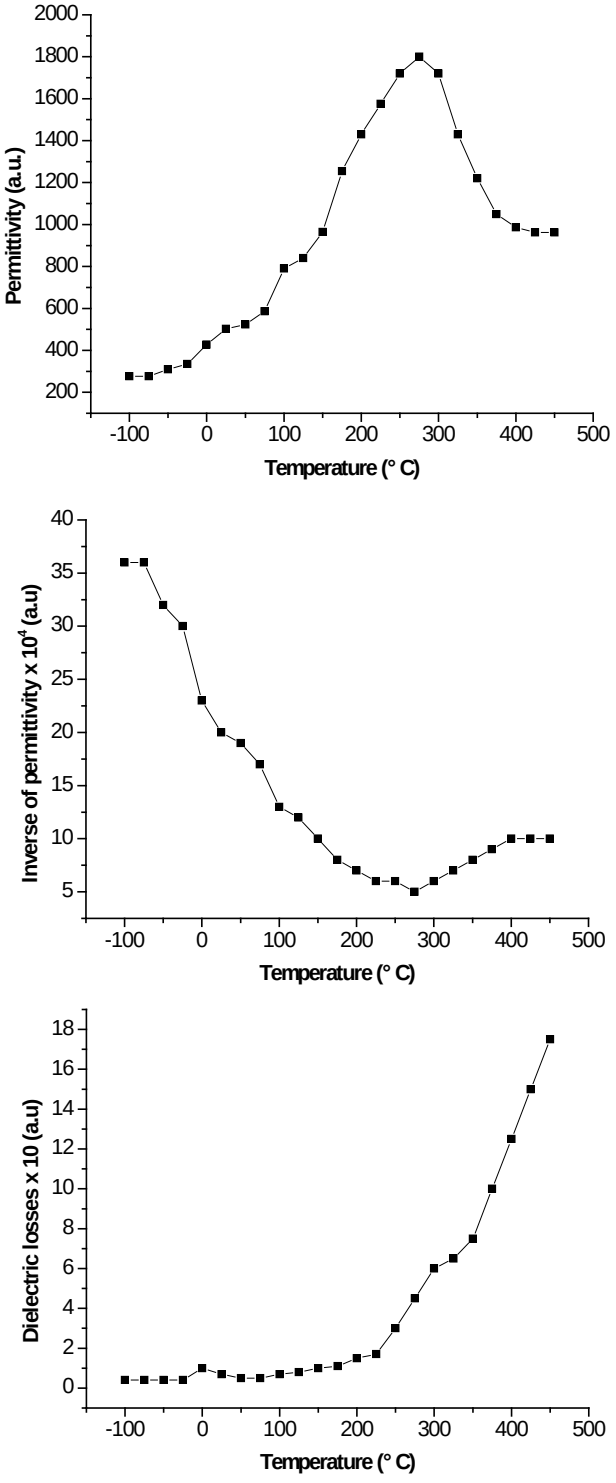

FIGURE 2 TEMPERATURE DEPENDENCE OF THE REAL PERMITTIVITY ε'_R , ITS INVERSE ε'^{-1}_R AND THE DIELECTRIC LOSSES TANδ AT 1KHZ FOR CERAMIC $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$

The two phase transitions above room temperature at T_2 and T_C have been confirmed by DTA, DSC and XRD analyses. Fig. 3 shows the DTA thermogram of the oxyfluoride on heating. Two slight anomalies are

detected on the curve at 183 ° C and 277 ° C respectively. Table I sums up the transition temperatures observed from the various techniques used.

A difference is observed in the values obtained by the various methods used (175 °C ≤ T_2 ≤ 202 ° C; 271 ° C ≤ T_C ≤ 289 ° C on heating). Whatever the method used, T_2 and T_C are higher on heating than on cooling. This thermal hysteresis between the values of transition temperatures on heating and cooling is characteristic of first order phase transitions. This result is in agreement with the discontinuous variation of ε'^{-1}_r versus temperature shown in Fig. 2.

TABLE I PHASE TRANSITIONS TEMPERATURES OF $K(NB_{0.8}MG_{0.2})O_{2.4}F_{0.6}$

Methods	**T_1 (° C)**	**T_2 (° C)**	**T_C (° C)**
DE on heating	43 ± 10	175 ± 10	285 ± 5
DE on cooling	25 ± 10	125 ± 10	270 ± 5
DTA on heating	-	183 ± 5	277 ± 5
DTA on cooling	-	162 ± 5	256 ± 5
DSC on heating	-	202 ± 5	289 ± 5
DSC on cooling	-	192 ± 5	277 ± 5
XRD on heating	-	179 ± 10	274 ± 10

The doping effect on the phase transitions of $KNbO_3$ single crystals or ceramics was discussed in many studies. As reported in these papers, the substitutions in K-sites or Nb-sites by various ions have an influence on the phase transitions temperatures of the host lattice but seem to have no effect on its sequence of structural changes.

To have more details on the structural changes induced by the substitution of Mg^{2+} to Nb^{5+} and of F^- to O^{2-}, several attempts were made to grow $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ single crystals but without success. The obtained crystals were too small and of bad quality. Therefore, we performed Guinier Simon analyses on crushed ceramics. Fig. 4 reports the variation of the unit cell parameters with temperature.

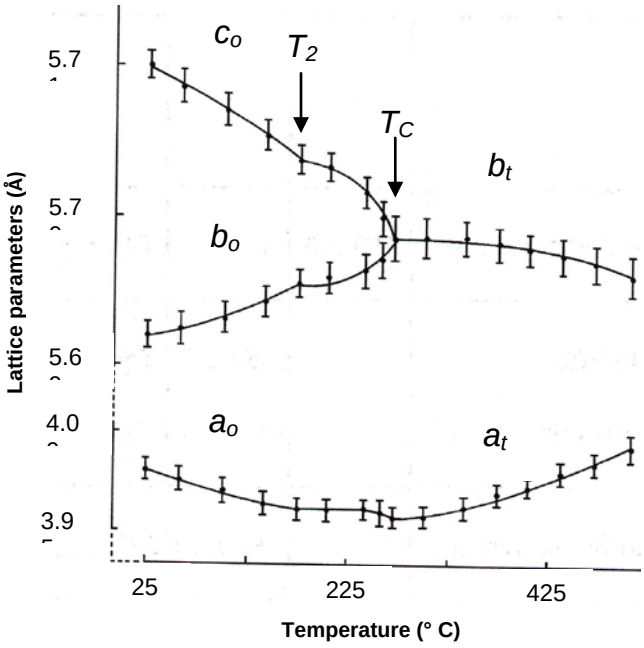

FIGURE 4 TEMPERATURE DEPENDENCE OF THE UNIT CELL PARAMETERS A, B AND C FOR $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$

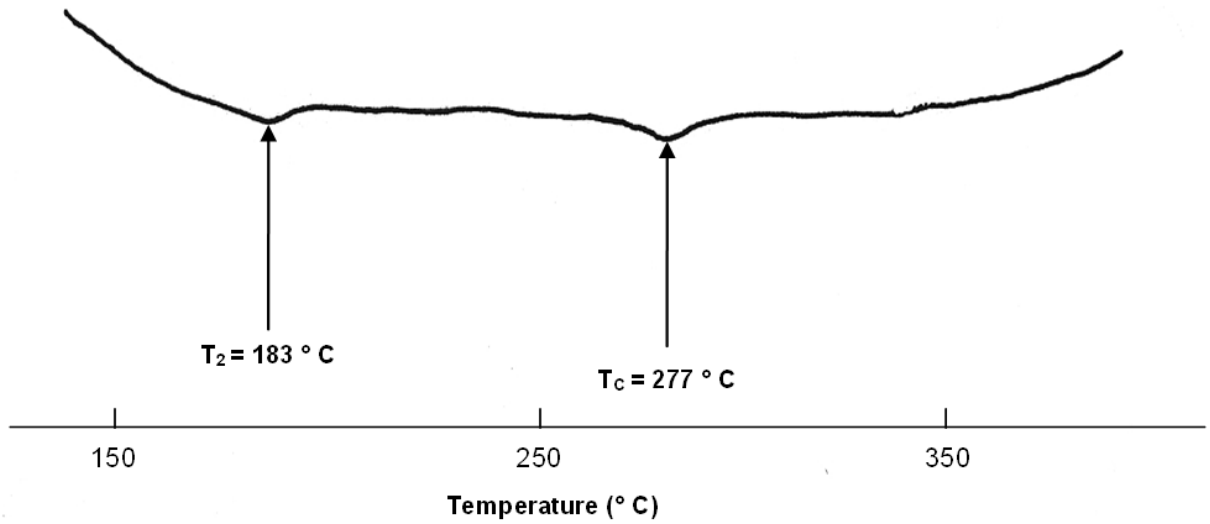

FIG. 3 DTA THERMOGRAM OF $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$

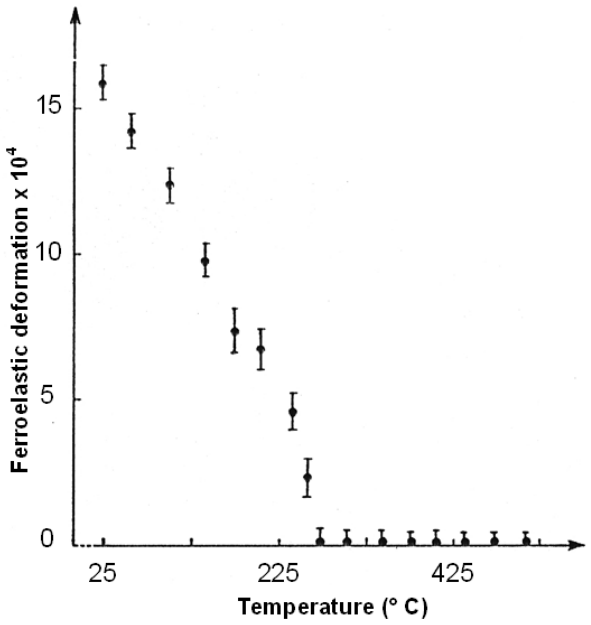

FIGURE 5 SPONTANEOUS DEFORMATION OF $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$

As we can see on Fig. 4, the thermal plots of a, b and c display two structural changes; the first one is around 180 ° C and the second one at about 275 ° C. The first transformation maintains the orthorhombic distortion of $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ perovskite whereas the second one transforms the lattice symmetry from orthorhombic to tetragonal. The paraelectric phase is cubic in the host lattice $KNbO_3$ and tetragonal in the oxyfluoride $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$.

As a result, in contrast with previous works on substituted $KNbO_3$ where the various substitutions didn't affect at all the orthorhombic-tetragonal-cubic sequence of structural changes in the host lattice, in our study, this sequence is broken and replaced by the following one: orthorhombic-orthorhombic–tetragonal, as seen in Fig. 4.

Below T_2 the lattice symmetry is orthorhombic. At T_2, the soft mode displacements of Mg^{2+} and Nb^{5+} ions from the centrosymmetric positions along the polar two-fold axis induce probably a change in the space group of the unit cell without any transformation in the lattice symmetry which remains orthorhombic. With increasing temperature, the order–disorder mode increases in the phase transitions mechanism as suggested in many studies.

Between T_2 and T_C, in addition to the displacements of Mg^{2+} and Nb^{5+} in the octahedra, the order – disorder increases gradually in the crystallographic positions of these ions leading, at T_C, to a centrosymmetric lattice with a tetragonal paraelectric phase. Therefore, the phase transition at T_C is probably due to a transition from the polar point group mm2 of the orthorhombic phase to the centrosymmetric point group 4/mmm of the tetragonal phase.

Fig. 5 gives the spontaneous deformation versus temperature $e_s = (c_o - b_o) / (c_o + b_o)$ where b_o and c_o represent the lattice parameters of the orthorhombic phase. As seen, e_s decreases continuously between room temperature and the Curie temperature. Above T_C, the symmetry becomes tetragonal with $c_o = b_o = b_t$ and therefore the spontaneous deformation disappears ($e_s = 0$). The value of e_s at room temperature is 1.6×10^{-3}.

Conclusions

The sinterability of potassium niobate at 900° C has been improved with an addition of 20 mol. % of $KMgF_3$ to 80 mol. % of $KNbO_3$. The volatilization of K_2O has been avoided owing to the sintering process in sealed tubes and consequently the chemical composition of the obtained ceramic is $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ without any incorporation of OH^- ions in the crystallographic lattice. Like pure $KNbO_3$, the fluorinated ceramic exhibits three phase transitions. The double substitution Nb^{5+} - Mg^{2+} and O^{2-} - F^- increases the phase transition temperature below room temperature and decreases the two phase transitions temperatures above room temperature. The Curie temperature is significantly lowered from 435 ° C to ~ 270 ° C. Moreover, contrariwise to previous works on substituted $KNbO_3$ where the sequence of structural changes of potassium niobate is maintained, in this study, the sequence orthorhombic - tetragonal - cubic is transformed into the orthorhombic - orthorhombic - tetragonal one. Thus, the paraelectric phase is tetragonal in $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ whereas it is cubic in pure $KNbO_3$. This new ceramic is a promising lead-free material in the manufacture of various electronic devices and particularly for electromechanical conversion owing to its dielectric characteristics. Besides, $K(Nb_{0.8}Mg_{0.2})O_{2.4}F_{0.6}$ bulk ceramic could be used as a target in thin films deposition.

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